AD

TECHNICAL REPORT ARCCB-TR-96006

EPITAXIAL QUALITY OF THIN Ag FILMS ON GaAs(100) SURFACES CLEANED WITH VARIOUS WET ETCHING TECHNIQUES

K. E. MELLO
S. R. SOSS
S. P. MURARKA
T. M. LU
S. L. LEE

MARCH 1996

US ARMY ARMAMENT RESEARCH,
DEVELOPMENT AND ENGINEERING CENTER
CLOSE COMBAT ARMAMENTS CENTER
BENÉT LABORATORIES
WATERVLIET, N.Y. 12189-4050

APPROVED FOR PUBLIC RELEASE; DISTRIBUTION UNLIMITED

DISCLAIMER

The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents.

The use of trade name(s) and/or manufacturer(s) does not constitute an official indorsement or approval.

DESTRUCTION NOTICE

For classified documents, follow the procedures in DoD 5200.22-M, Industrial Security Manual, Section II-19 or DoD 5200.1-R, Information Security Program Regulation, Chapter IX.

For unclassified, limited documents, destroy by any method that will prevent disclosure of contents or reconstruction of the document.

For unclassified, unlimited documents, destroy when the report is no longer needed. Do not return it to the originator.

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	March 1996	Final

4. TITLE AND SUBTITLE

EPITAXIAL QUALITY OF THIN Ag FILMS ON GaAs(100) SURFACES CLEANED WITH VARIOUS WET ETCHING TECHNIQUES

5. FUNDING NUMBERS

AMCMS No. 6226.24.H180.0
PRON No. TU5B5F261ABJ

6. AUTHOR(S)

K.E. Mello (RPI, Troy, NY), S.R. Soss (RPI),
S.P. Murarka (RPI), T.M. Lu (RPI), and S.L. Lee

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

U.S. Army ARDEC
Benet Laboratories, AMSTA-AR-CCB-O
Watervliet, NY 12189-4050

8. PERFORMING ORGANIZATION REPORT NUMBER

ARCCB-TR-96006

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

U.S. Army ARDEC
Close Combat Armaments Center
Picatinny Arsenal, NJ 07806-5000

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

Submitted to *Applied Physics Letters*.

12a. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for public release; distribution unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

Two theta scans and pole figure X-ray analyses have been used to examine the crystal structure and orientation of Ag films deposited on GaAs(100) substrates cleaned by a variety of wet etches. Where epitaxy was observed, it was of the type Ag(110)/GaAs(100). The H_3PO_4/HCl sequential etch yielded the film with the highest degree of preferred orientation, with the H_2SO_4/HCl, NH_4OH, and HF etches producing films of decreasing quality in the order named. The epitaxial quality is thought to scale with elemental As concentration on the GaAs(100) surface, and have an inverse relationship to the amount of surface oxides present before deposition.

14. SUBJECT TERMS

Epitaxial Growth, Surface Cleaning, Chemical Etching

15. NUMBER OF PAGES

11

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	UL

TABLE OF CONTENTS

TABLES

LIST OF ILLUSTRATIONS

ACKNOWLEDGEMENTS

This work was supported by the National Science Foundation, grant number NSF ECS-9310613. We thank G. R. Yang for performing the XPS experiments.

INTRODUCTION

The nature and quality of metal/semiconductor interfaces are of considerable importance in device applications. The thickness and nature of surface oxides can have a significant impact on Schottky diode behavior and ohmic contact formation.[1-2] A number of wet cleaning procedures have been developed to prepare semiconductor substrates for molecular-beam epitaxy (MBE) growth and for device fabrication.[1,3,4] Generally, the treated GaAs surface should be smooth, have no metallic contaminants, be free of oxides, and have a Ga/As ratio of unity. Often, the cleaning procedure begins with a degreasing cycle in which the wafer is immersed in hot acetone and methanol, and rinsed in DI water. The wafer surface is then oxidized by an oxidizing agent (typically OH- from H_2O_2) to produce As_2O_3, As_2O_5, Ga_2O_3, $Ga_2O_3(H_2O)$, and the Ga suboxide Ga_2O. Finally, the oxidation products are removed by an acid or a base. Typically, both the acid or base and the H_2O_2 are in solution, and the oxide formation and removal occur simultaneously. Acids used include sulfuric (H_2SO_4), phosphoric (H_3PO_4), citric ($C_6H_8O_7$), hydrochloric (HCl), and hydrofluoric (HF). HF buffered with ammonium fluoride (FH_4N) is also used. Surface oxides and contaminants present after wet etching have been studied mainly by X-ray photoelectron spectroscopy (XPS).[2,5,6]

The quality of epitaxial thin films is extremely sensitive to the surface condition immediately prior to deposition. This report investigates the orientational characteristics of thin Ag films on GaAs(100) substrates cleaned by various wet-etching techniques. Two theta scans and pole figure X-ray analyses on the Ag/GaAs(100) samples were performed to determine the crystal structure of the Ag overlayers and any epitaxial orientations of the films to the GaAs(100) substrates. The substrates were cleaned with various wet-etching schemes using phosphoric, sulfuric, hydrochloric, and hydrofluoric acid-based etches and an ammonium hydroxide etch.

EXPERIMENTAL PROCEDURE

The substrate in all cases was an *n*-doped GaAs(100) wafer prepared using four different cleaning techniques as shown in Table 1. The partially ionized beam (PIB) deposition technique used to deposit the Ag films has been previously described.[7] Briefly, a small fraction (0-5%) of the evaporated species is ionized by the electrons used to heat the crucible by electron bombardment. The self ions are then accelerated toward the substrate by an accelerating potential difference between the crucible and substrate and are deposited along with the neutral species. Deposition conditions were: substrate at room temperature; base pressure less or equal to $2x10^{-5}$ Pa; deposition rate approximately equal to 4.0 angstroms/sec; and final film thickness approximately equal to 800 angstroms. All depositions were carried out with a "floating" substrate potential, in which the substrate is left electrically isolated during deposition. The "floating" condition was seen previously to optimize epitaxial Ag film quality in our PIB deposition system.[12] The floating substrate potential represents a unique situation. Due to the 600-1,000 V positive bias on the crucible present for electron bombardment heating, ions are definitely present in the beam and are repelled to all areas of the chamber at a lower potential, including the substrate. However, because the substrate rapidly charges up due to ion impact, the ions enter into the film growth mainly in the initial stages. This is precisely the stage at

which they would be most helpful in facilitating epitaxial growth because of their ability to provide additional energy to the growth front and sputter away light impurities on the substrate surface.[8-10]

After growth, the samples were characterized using a Scintag X-ray diffraction system 2000. Two theta scans determined the grains present in the film, while a pole figure analysis determined the azimuthal orientation of these grains relative to the substrate. In the pole figure analysis[11], a two theta angle is set for the plane of interest, then the sample is tilted incrementally from 0° to 80°. At each increment the sample is rotated 360° azimuthally (see Figure 1). The result is a stereogram that reveals the poles (or normals) from each plane in the family. If the stereogram contains rings of intensity, the planes are randomly oriented in the film, whereas spots (or poles) of intensity reveal a preferred orientation in the film and give their exact azimuthal orientation. Comparing the stereograms of the substrate and film determines the exact orientation of the film relative to the substrate.

OBSERVATIONS

The epitaxy observed in all cases was Ag(110)/GaAs(100). However, the epitaxial quality varies with the cleaning technique employed. The H_3PO_4/HCl sequential etch has the smallest Ag(111)/Ag(110) two theta intensity ratio, followed by the H_2SO_4/HCl etch, and finally the NH_4OH and HF etches. Thus, the sample cleaned with the H_3PO_4/HCl sequential etch has the largest portion of Ag(110) grains, and the HF sample the smallest. These results are summarized in Table 2 and Figure 2. The stereograms of Figure 3 show the Ag(111) poles present in the film. Only the Ag(111) poles were examined because reflections from Ag(200) and GaAs(220) occur at nearly the same two theta angle. The same is true for the Ag(220) and GaAs(400) reflections. When probing the Ag(100) and Ag(110) poles, only the more powerful substrate reflections occur in the stereograms. The predominant (111) poles in the stereograms of Figure 3 occur at 35.3°: the Ag(111) poles from the Ag(110) grains. In principle, one should see poles at 35.3° with two-fold symmetry and poles at 90° with four-fold symmetry. The poles at 90° are not observed because the χ-tilt angle is restricted to 80°.

In the H_3PO_4/HCl etched sample, the poles at 35.3° are very sharp and tight, indicating that the Ag(110) grains have little tilt grain-to-grain and are all similarly azimuthally oriented. The Ag(111) poles of the H_2SO_4/HCl etched sample are broader, indicating a less exact orientation of the Ag(110) grains. The NH_4OH etched sample is poorer still. In the stereogram of the HF etched sample, there are no Ag(111) poles at 35.3°, because little to no Ag(110) grains are present in the film. Instead, a large central (111) pole is present, indicating that the primary grains present are Ag(111), as is clearly seen in the two theta scan of the HF etched sample in Figure 2. The uniform intensity in other areas of the stereogram shows that these (111) planes are stacked randomly and have no preferred azimuthal orientation.

Another more simple view is presented in Figure 4. These "chi" scans are obtained by fixing the tilt angle and rotating the sample 360° azimuthally. For Ag(110) on GaAs(100), the two theta angle was first set to the (111) poles of Ag; the sample normal was then tilted by 35.3°

to the diffractometer plane, which corresponds to the angle between the (111) and (110) planes in a cubic crystal. The azimuthal scan was then performed by rotating the sample 360°. For the substrate, the two theta angle was set to the GaAs(111) poles and the tilt-angle to 54.7°, which corresponds to the angle between the (100) and (111) planes of the cubic structure, then an azimuthal scan was similarly performed. The GaAs wafer reflects four (111) peaks under rotation through 360°, since there are four equivalent (111) poles in the (100) projection. Because the two peaks from the Ag(111) poles align with two of the (111) poles of the GaAs(100) substrate, the azimuthal character of the epitaxy is revealed.

High-quality epitaxial Ag(110) films on GaAs(100) surfaces can be obtained with an HF dip.[12] This work was previously reported in Reference 12. The essentially non-epitaxial film obtained here had the same HF dip, but was subsequently rinsed in DI water. It is known that GaAs(100) etched in HF and blow-dried in N_2 yields an oxide thickness of only about 12 angstroms.[1] Presumably the DI water rinse increases the oxide layer thickness, although this is reported not to occur.[5] Controlling oxide thickness is important because in metallizing GaAs for ohmic contact formation and for nearly ideal Schottky diode behavior, the residual dielectric layer thickness must be reduced to a minimum. This suggests that, of the four techniques examined here, the H_3PO_4/HCl sequential etch applied to GaAs(100) provides the most favorable surface condition for the epitaxial growth of Ag. Lu et al.[2] conducted XPS studies of the GaAs(100) surface after the HP_3O_4/HCl and H_2SO_4/HCl sequential etches and found that the former left a more As-rich surface than the latter. In addition, it was noted that elemental As increased in concentration as the surface oxides decreased. A similar study by Olivier et al.[5] concluded that an NH_4OH etch left a more As-rich surface than an HF etch. Our own XPS studies of the substrates immediately after etching agree with the above and show that the HF etched sample has more surface As_2O_3 than the H_3PO_4/HCl etched sample. These results suggest that a wet etch can improve epitaxial quality in the Ag(110)/GaAs(100) system by leaving more elemental As on the surface. The more As-rich surfaces have less oxides present,[2] which may facilitate epitaxial growth.

CONCLUSION

In conclusion, it was found that thin Ag films deposited on GaAs etched with an H_3PO_4/HCl sequential etch provided the best epitaxial quality, followed by H_2SO_4/HCl, NH_4OH, and finally HF. A correlation was found between the epitaxial quality and probable elemental As concentration on the surface. These results suggest that the surface condition of GaAs(100) varies markedly with the cleaning technique employed. Thus, selecting the appropriate etching scheme (and corresponding surface condition) can favorably affect epitaxial formation condition, by controlling the orientation of the grown overlayer.

REFERENCES

1. Mukherjee, S. D., Woodward, D., in *Gallium Arsenide Materials, Devices and Circuits*, edited by M. J. Howes, D. V. Morgan, Wiley, New York, **1985**, pp. 123, 148-149.

2. Lu, Z. H., Lagarde, C., Sacher E., Currie, J. F., and Yelon, A., *J. Vac. Sci. Technol.* A 7, 3, **1989**.

3. Williams, R. E., *Gallium Arsenide Processing Techniques*, Artech, Massachusetts, **1984**, p. 93.

4. Sze, S. M., *VLSI Technology*, McGraw-Hill, New York, **1983**, p. 37.

5. Olivier, J., Landesman, J. P., and Wyczisk, F., Inst. Phys. Conf. Ser. No. 112, 305, **1990**.

6. Menda, K., Kanda, E., and Yokoyama, T., *Jap. J. Appl. Phys.* 29, L391, **1990**.

7. Mei, S. N., and Lu, T. M., *J. Vac. Sci. Technol.* A 6, 9, **1988**.

8. Yapsir, A. S., Lu, T. M., and Lanford, W. A., *Appl. Phys. Lett.* 52, 1962, **1988**.

9. Yang, G. R., Bai, P., Lu, T. M., and Lau, W. M., *J. Appl. Phys.* 66, 4519, **1989**.

10. Bai, P., Yang, G. R., and Lu, T. M., *J. Appl. Phys.* 68, 3619, **1990**.

11. Cullity, B. D., *Elements of X-ray Diffraction*, Addison-Wesley, Reading, Massachusetts, **1978**, p. 297.

12. Nason, T. C., You, L., and Lu, T. M., *Appl. Phys. Lett.* 60, 175, **1992**.

TABLE 1. Cleaning techniques employed. Each column represents the sequence of a particular cleaning procedure.

I	II	III	IV
Acetone, methanol, DI H_2O	Acetone, methanol, DI H_2O	Acetone, methanol, DI H_2O	Acetone, methanol, DI H_2O
H_3PO_4:H_2O_2:H_2O 1:10:10	H_2SO_4:H_2O_2:H_2O 1:8:80	NH_4OH:H_2O_2 1:700	HF:H_2O 20:1
HCL:H_2O 1:1	HCL:H_2O 1:1		
DI H_2O	DI H_2O	DI H_2O	DI H_2O
N_2 blow	N_2 blow	N_2 blow	N_2 blow

TABLE 2. X-ray peak intensity ratios.

Sample	Ag(111)/Ag(110) Two-Theta Intensity Ratio
I	0.082
II	0.32
III	1.4
IV	3.5

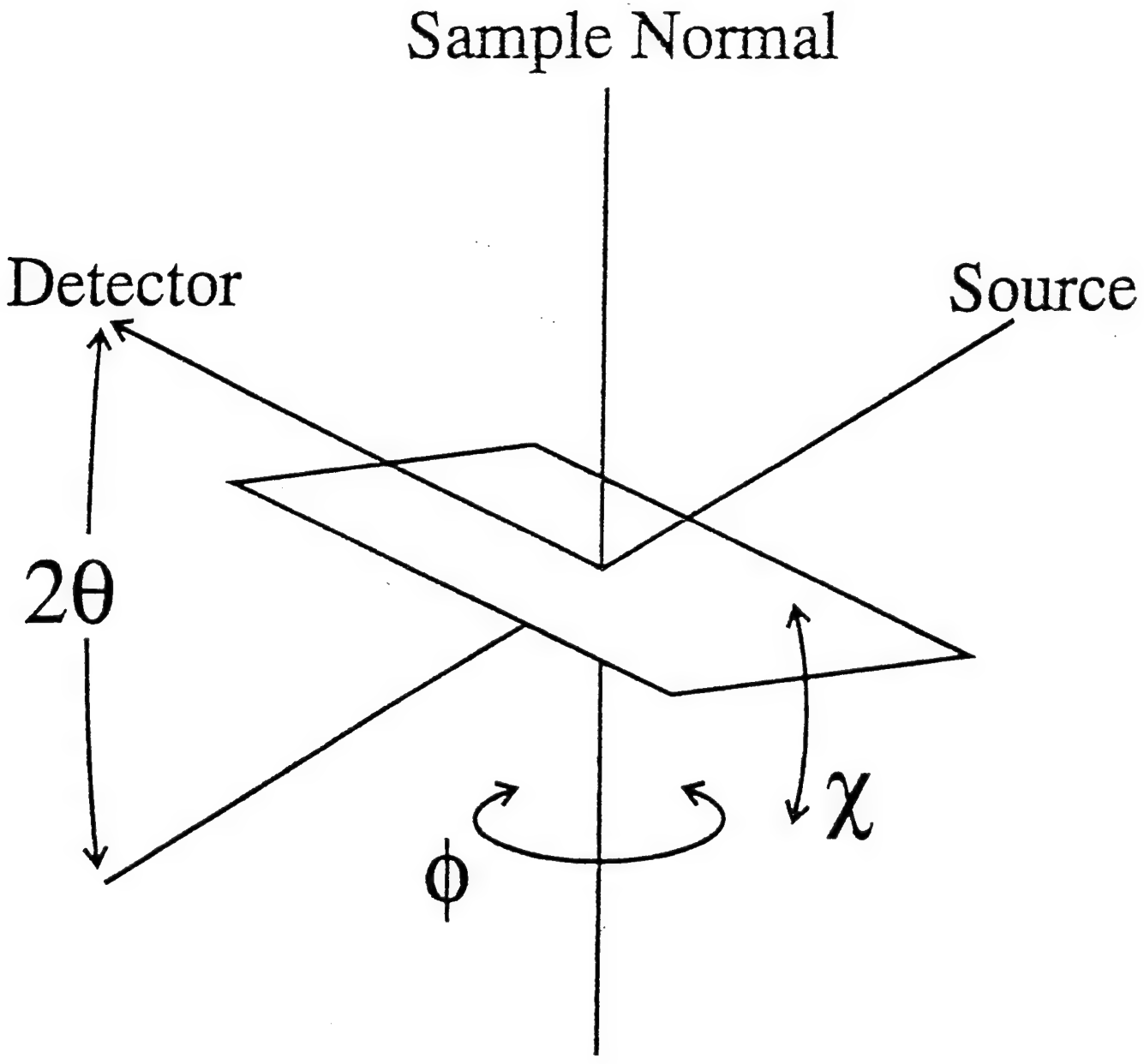

Figure 1 Specimen geometry relative to the x-ray source and detector, showing angles 2θ, χ, and azimuthal angle ϕ.

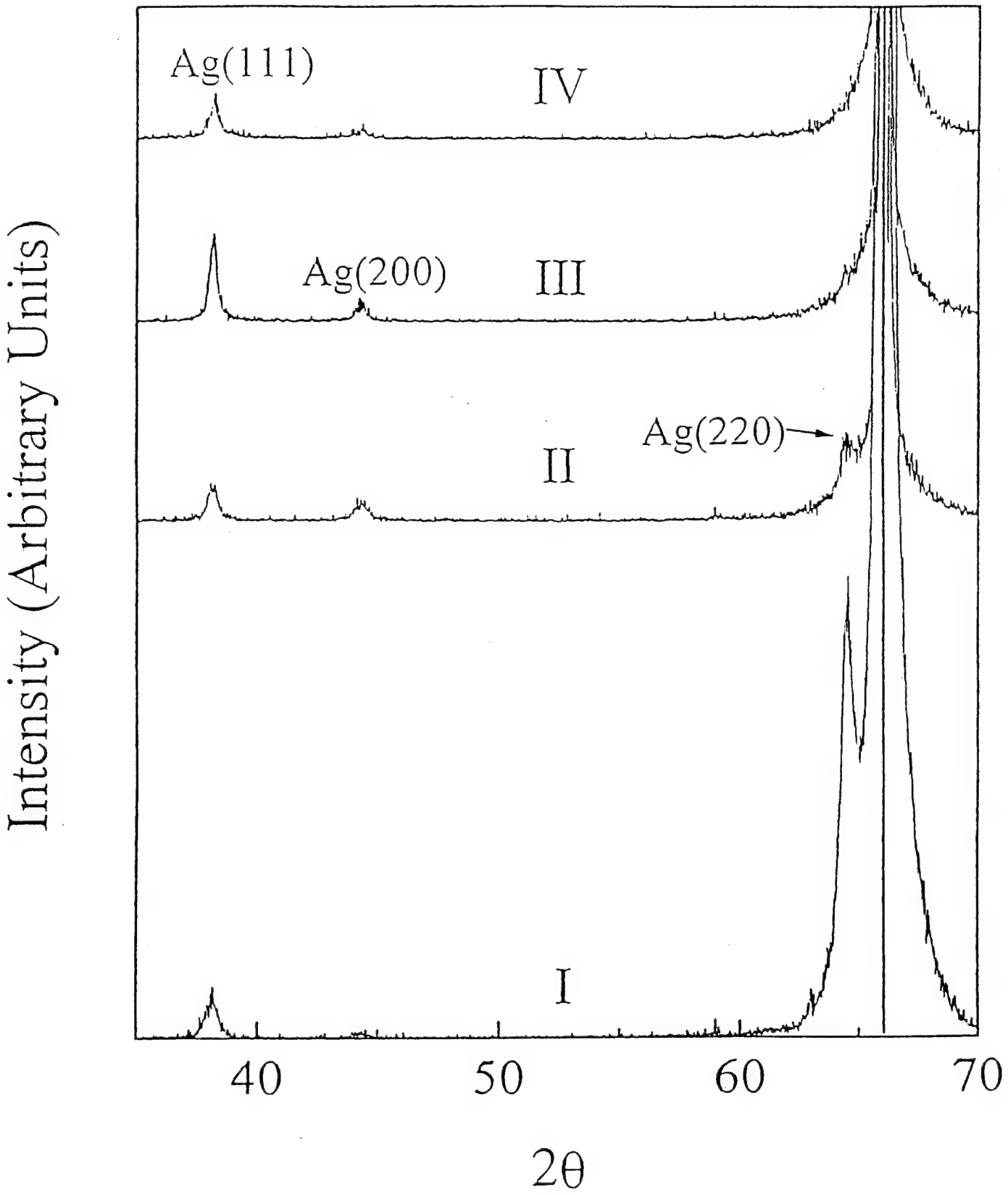

FIGURE 2. 2θ scans representing the four different wet etches of GaAs(100). All four Ag films had identical deposition conditions.

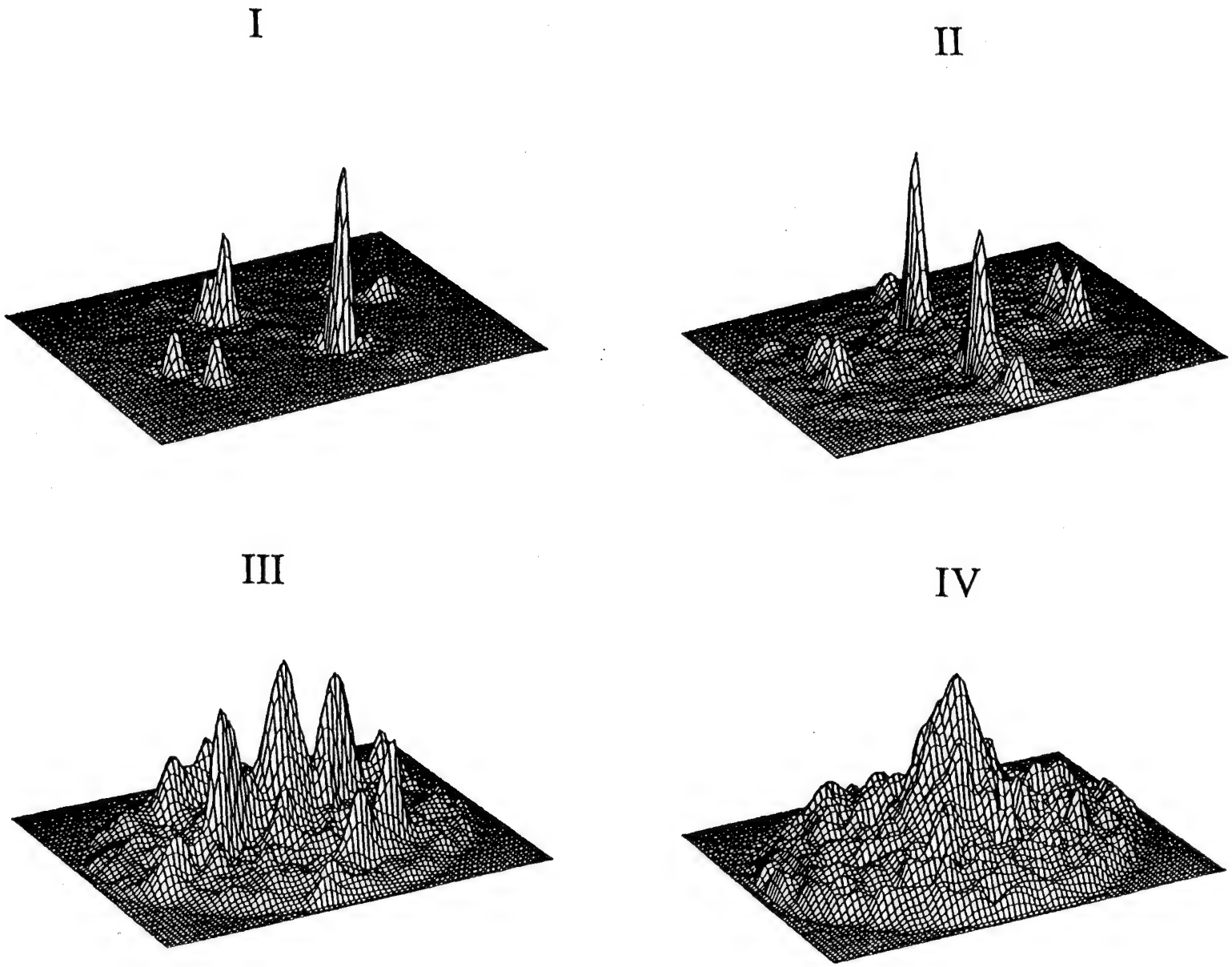

FIGURE 3. 3-D stereographic projections showing the Ag(111) poles. In samples I and II, the predominant poles present are from Ag(110) grains. In sample III, poles from Ag(110) and Ag(111) grains are visible (note the central (111) peak), whereas sample IV contains randomly oriented (111) grains almost exclusively.

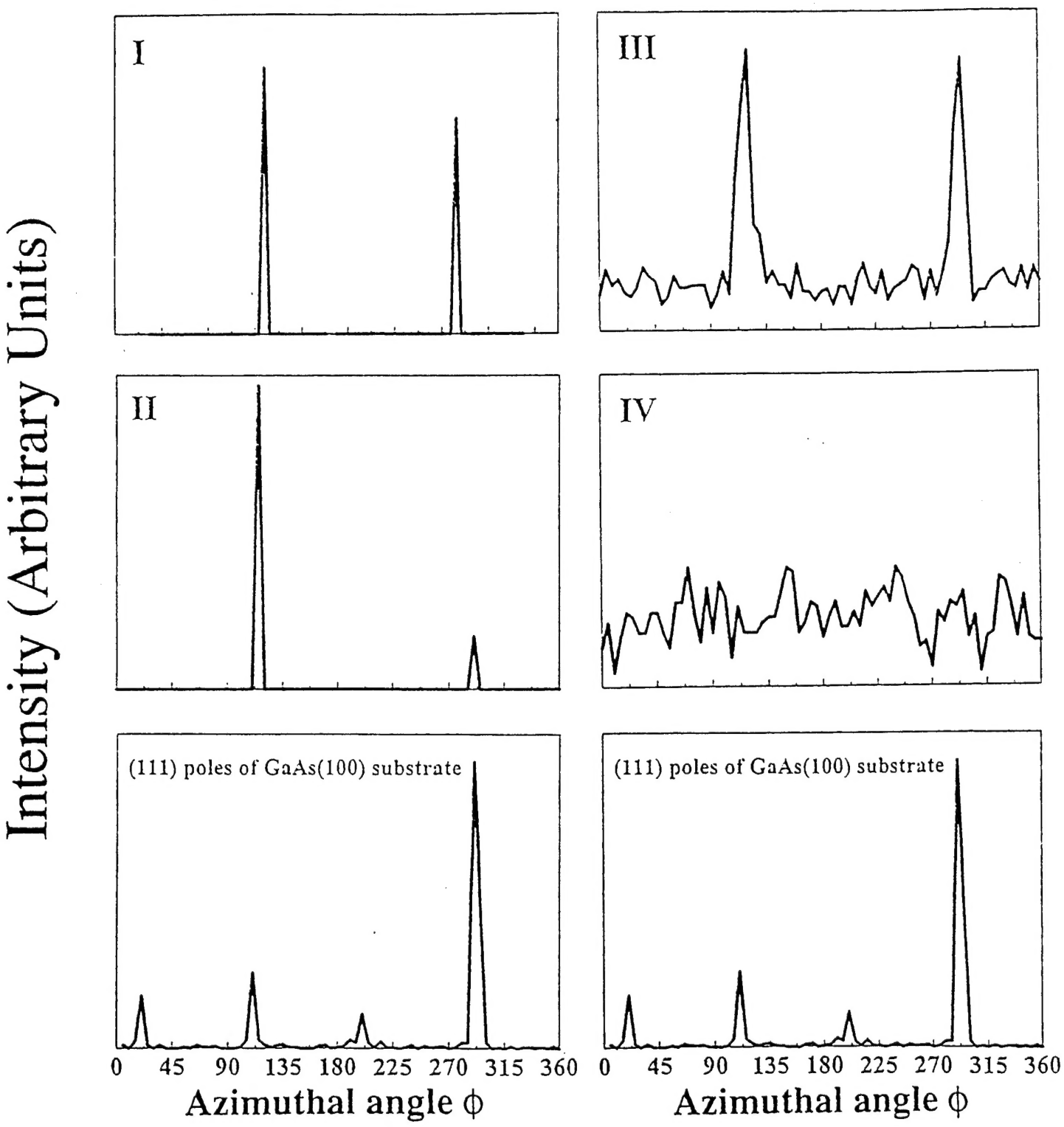

FIGURE 4. Ag(110) on GaAs(100) χ scans, showing the azimuthal character of the epitaxy using the four cleaning techniques.

TECHNICAL REPORT INTERNAL DISTRIBUTION LIST

	NO. OF COPIES
CHIEF, DEVELOPMENT ENGINEERING DIVISION	
ATTN: AMSTA-AR-CCB-DA	1
-DB	1
-DC	1
-DD	1
-DE	1
CHIEF, ENGINEERING DIVISION	
ATTN: AMSTA-AR-CCB-E	1
-EA	1
-EB	1
-EC	1
CHIEF, TECHNOLOGY DIVISION	
ATTN: AMSTA-AR-CCB-T	2
-TA	1
-TB	1
-TC	1
TECHNICAL LIBRARY	
ATTN: AMSTA-AR-CCB-O	5
TECHNICAL PUBLICATIONS & EDITING SECTION	
ATTN: AMSTA-AR-CCB-O	3
OPERATIONS DIRECTORATE	
ATTN: SIOWV-ODP-P	1
DIRECTOR, PROCUREMENT & CONTRACTING DIRECTORATE	
ATTN: SIOWV-PP	1
DIRECTOR, PRODUCT ASSURANCE & TEST DIRECTORATE	
ATTN: SIOWV-QA	1

NOTE: PLEASE NOTIFY DIRECTOR, BENÉT LABORATORIES, ATTN: AMSTA-AR-CCB-O OF ADDRESS CHANGES.

TECHNICAL REPORT EXTERNAL DISTRIBUTION LIST

	NO. OF COPIES
ASST SEC OF THE ARMY RESEARCH AND DEVELOPMENT ATTN: DEPT FOR SCI AND TECH THE PENTAGON WASHINGTON, D.C. 20310-0103	1
DEFENSE TECHNICAL INFO CENTER ATTN: DTIC-OCP (ACQUISITIONS) 8725 JOHN J. KINGMAN ROAD STE 0944 FT. BELVOIR, VA 22060-6218	2
COMMANDER U.S. ARMY ARDEC ATTN: AMSTA-AR-AEE, BLDG. 3022	1
AMSTA-AR-AES, BLDG. 321	1
AMSTA-AR-AET-O, BLDG. 183	1
AMSTA-AR-FSA, BLDG. 354	1
AMSTA-AR-FSM-E	1
AMSTA-AR-FSS-D, BLDG. 94	1
AMSTA-AR-IMC, BLDG. 59 PICATINNY ARSENAL, NJ 07806-5000	2
DIRECTOR U.S. ARMY RESEARCH LABORATORY ATTN: AMSRL-DD-T, BLDG. 305 ABERDEEN PROVING GROUND, MD 21005-5066	1
DIRECTOR U.S. ARMY RESEARCH LABORATORY ATTN: AMSRL-WT-PD (DR. B. BURNS) ABERDEEN PROVING GROUND, MD 21005-5066	1
DIRECTOR U.S. MATERIEL SYSTEMS ANALYSIS ACTV ATTN: AMXSY-MP ABERDEEN PROVING GROUND, MD 21005-5071	1

	NO. OF COPIES
COMMANDER ROCK ISLAND ARSENAL ATTN: SMCRI-SEM ROCK ISLAND, IL 61299-5001	1
MIAC/CINDAS PURDUE UNIVERSITY 2595 YEAGER ROAD WEST LAFAYETTE, IN 47906-1398	1
COMMANDER U.S. ARMY TANK-AUTMV R&D COMMAND ATTN: AMSTA-DDL (TECH LIBRARY) WARREN, MI 48397-5000	1
COMMANDER U.S. MILITARY ACADEMY ATTN: DEPARTMENT OF MECHANICS WEST POINT, NY 10966-1792	1
U.S. ARMY MISSILE COMMAND REDSTONE SCIENTIFIC INFO CENTER ATTN: AMSMI-RD-CS-R/DOCUMENTS BLDG. 4484 REDSTONE ARSENAL, AL 35898-5241	2
COMMANDER U.S. ARMY FOREIGN SCI & TECH CENTER ATTN: DRXST-SD 220 7TH STREET, N.E. CHARLOTTESVILLE, VA 22901	1
COMMANDER U.S. ARMY LABCOM, ISA ATTN: SLCIS-IM-TL 2800 POWER MILL ROAD ADELPHI, MD 20783-1145	1

NOTE: PLEASE NOTIFY COMMANDER, ARMAMENT RESEARCH, DEVELOPMENT, AND ENGINEERING CENTER, BENÉT LABORATORIES, CCAC, U.S. ARMY TANK-AUTOMOTIVE AND ARMAMENTS COMMAND, AMSTA-AR-CCB-O, WATERVLIET, NY 12189-4050 OF ADDRESS CHANGES.

TECHNICAL REPORT EXTERNAL DISTRIBUTION LIST (CONT'D)

	NO. OF COPIES
COMMANDER U.S. ARMY RESEARCH OFFICE ATTN: CHIEF, IPO P.O. BOX 12211 RESEARCH TRIANGLE PARK, NC 27709-2211	1
DIRECTOR U.S. NAVAL RESEARCH LABORATORY ATTN: MATERIALS SCI & TECH DIV WASHINGTON, D.C. 20375	1
WRIGHT LABORATORY ARMAMENT DIRECTORATE ATTN: WL/MNM EGLIN AFB, FL 32542-6810	1
WRIGHT LABORATORY ARMAMENT DIRECTORATE ATTN: WL/MNMF EGLIN AFB, FL 32542-6810	1

NOTE: PLEASE NOTIFY COMMANDER, ARMAMENT RESEARCH, DEVELOPMENT, AND ENGINEERING CENTER, BENÉT LABORATORIES, CCAC, U.S. ARMY TANK-AUTOMOTIVE AND ARMAMENTS COMMAND, AMSTA-AR-CCB-O, WATERVLIET, NY 12189-4050 OF ADDRESS CHANGES.